Nature of the reversible paramagnetism to ferromagnetism state in cobalt-doped titanium dioxide

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We report that $Co_{0.1}Ti_{0.9}O_{2-\delta}$ prepared by the sol-gel technique is a paramagnet following the Curie–Weiss law: $\chi = \chi_0 + C/(T+\theta)$ with $\theta \simeq 5$ K. However, hydrogenation at 673 K in H_2/Ar (5%/95%) gas converts a part of the paramagnetic (P) sample to room temperature ferromagnet (RTFM) and reheating the sample at 573 K in air converts it back to a paramagnet completely. This reversible $P \rightleftarrows$ RTFM transition has been observed for additional cycles by alternately heating in air and H_2/Ar. It is argued that this RTFM is intrinsic and it is due to Co^{2+}–Co^{2+} exchange interaction mediated by oxygen holes which are produced by hydrogenation but eliminated by oxidation. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1854931]

Reports of RTFM (room temperature ferromagnetism) in thin films of $Co_xTi_{1-x}O_{2-\delta}$ in 2001 by Matsumoto *et al.*[1] has aroused a great deal of interest as to the nature of the FM state since the FM state has been observed even for $x=0.01$. Soon after, Chambers *et al.*[2] reported RTFM in both epitaxial and polycrystalline Co-doped TiO_2 (anatase) films, followed by Park *et al.*[3] and Matsumoto *et al.*[4] reporting RTFM in Co-doped TiO_2 (rutile) films. More recent studies of these films by Punnoose *et al.*[5] using careful temperature dependence studies of magnetic behavior for different x values, by EMR (electron magnetic resonance) studies of Rameev *et al.*[6] and by Kim *et al.*[7] have shown that RTFM is most likely due to metallic Co nanoparticles. The controversy, however, is not yet completely resolved since the group of Shutthanandan *et al.*[8] have recently reported RTFM in ion-implanted Co-doped TiO_2 (rutile) films with $x \simeq 0.02$ without any evidence for the presence of metallic Co^0 state. Theoretically, Park *et al.*[9] proposed a model of RTFM in $Co_xTi_{1-x}O_{2-\delta}$ (Ref. 9) in which oxygen holes near Co can provide the necessary exchange coupling between Co^{2+} ions, leading to intrinsic RTFM.

In recent studies, we have taken somewhat different approaches to the synthesis of Co-doped TiO_2 samples. In one study,[10] thin films of Co/TiO_2 (anatase) prepared by spray pyrolysis were found to be paramagnetic in that the magnetic susceptibility followed the Curie–Weiss law: $\chi = \chi_0 + C/(T+\theta)$ with $\theta \simeq 5$ K and the magnitude of C consistent with the Co^{2+} state. Only for $T < 5$ K, some deviations from the paramagnetism were observed. In a more recent study,[11] we prepared $Co_{0.1}Ti_{0.9}O_{2-\delta}$ (anatase) powder by the sol-gel technique and found it to be paramagnetic in the 2–370 K range with $\mu = 4.1$ μ_B for the Co^{2+} ion. This is consistent with the high spin state of the Co^{2+} ion which substitutes for Ti^{4+} ions, with the balance of the charge compensated by $O_{2-\delta}$. We also showed that this sample, when hydrogenated at 573 K in pure H_2 gas, acquires RTFM with $T_c \simeq 470$ K.

Here we report that this acquired RTFM in the hydrogenated sample is reversible to paramagnetism (P) if the

sample is reheated in air (oxygen) at 573 K. Subsequent hydrogenation at 673 K produces RTFM again, confirming the reversible nature of FM $\rightleftarrows P$ state. We also report EMR (electron magnetic resonance) studies of these samples which confirm an EMR line due to the Co^{2+} state in the P state and a broad EMR line in the FM state. Details of these results and their discussions are presented below.

The procedures for the synthesis of the sol-gel samples of $Co_{0.1}Ti_{0.9}O_{2-\delta}$ are described in our recent paper.[11] For hydrogenation experiments, we followed a slightly different procedure in that hydrogenation was carried out in a H_2/Ar (5%/95%) mixture using a thermogravimetric analysis microbalance by maintaining the pelleted sample temperature at 673 K for 5 h (the H_2/Ar mixture is safer to handle than pure H_2). After hydrogenation, the sample was cut into two pieces and one piece was reheated in air at 673 K for 6 h. After completing magnetic studies on this reheated sample, this sample was rehydrogenated using the same procedure. Here we present data on these three samples: sample 1 (first hydrogenation); sample 2 (reheated in air); and sample 3 (rehydrogenation). Studies reported here include room temperature x-ray diffraction (XRD) using Cu K_α radiation with $\lambda = 0.15418$ nm, temperature (T), and magnetic field (H) dependence of the magnetization M and the magnetic susceptibility $\chi = M/H$ using a commercial superconducting quantum interference device magnetometer and EMR studies at 5 K and frequency $f = 9.28$ GHz using a conventional spectrometer.

In Fig. 1 the room temperature XRD patterns of samples 1, 2, and 3 described above are shown. Although anatase is the dominant phase, small amounts of the rutile and brookite phase of TiO_2 are also present. The room temperature M versus H variations for the samples 1 and 2 are shown in Fig. 2, with the inset showing the full hysteresis-loop for sample 3 whose magnetization is much larger than that of sample 1 obtained after first hydrogenation. It is evident that hydrogenated samples 1 and 3 have a FM component although to different degrees whereas sample 2 obtained by heating sample 1 in air is completely paramagnetic just like the parent sample discussed in detail in Ref. 11. The larger value of

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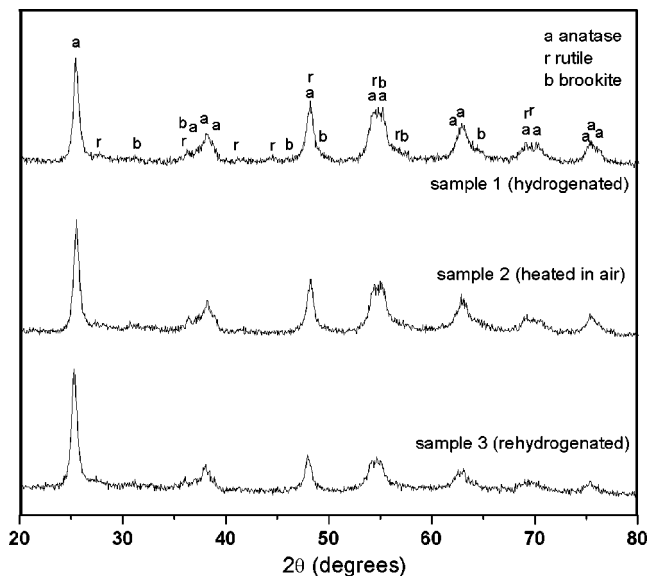[a)]Electronic mail: amanivan@wvu.edu

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FIG. 1. Room temperature XRD patterns of sample 1 (hydrogenated), sample 2 (heated in air), and sample 3 (rehydrogenated). The expected positions of the Bragg lines for the three forms of TiO$_2$ are shown.

FIG. 3. *M-H* plot of sample 1 at 300 and 5 K, with the inset showing the full loop at 5 K. H_c is the coercivity.

M for sample 3 (as compared to sample 1) is most likely due to its more complete hydrogenation because of smaller size, i.e., a large fraction of sample 3 has undergone transformation to the FM state. On the other hand, only a small fraction (mainly surface) of sample 1 is ferromagnetic, the rest being still paramagnetic. This is evident from the *M* versus *H* data of Fig. 3 taken at 5 and 300 K in which the higher *H* linear behavior is due to the *P* component.

To establish the paramagnetic nature of the reheated (in air) sample 2, we show its χ versus *T* variation in Fig. 4, with the inset showing the *M* versus *H* variations at 300 and 2 K. The χ-*T* variation fits the Curie–Weiss law (solid line) with $C=1.76 \times 10^{-3}$ emu K/g Oe, $\chi_0=4.55 \times 10^{-6}$ emu/g Oe and $\theta=5$ K, quite similar to the behavior of the parent sol-gel prepared sample discussed in Ref. 11. The non-linear *M* versus *H* curve of Fig. 4 at 2 K, without the presence of a hysteresis, is characteristic of the Brillouin-type variation ex-
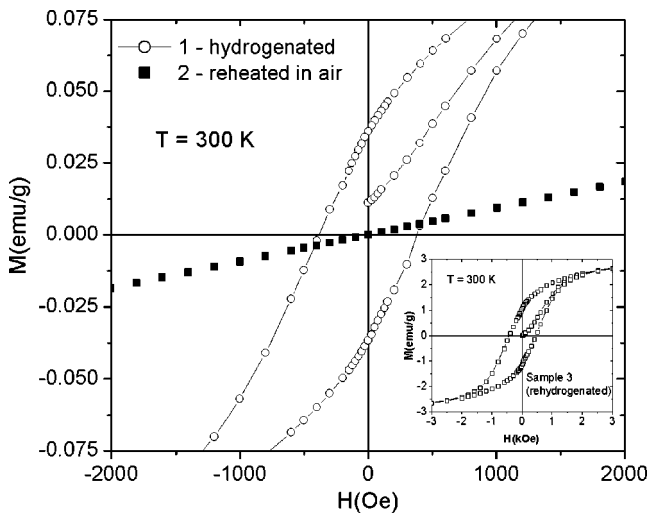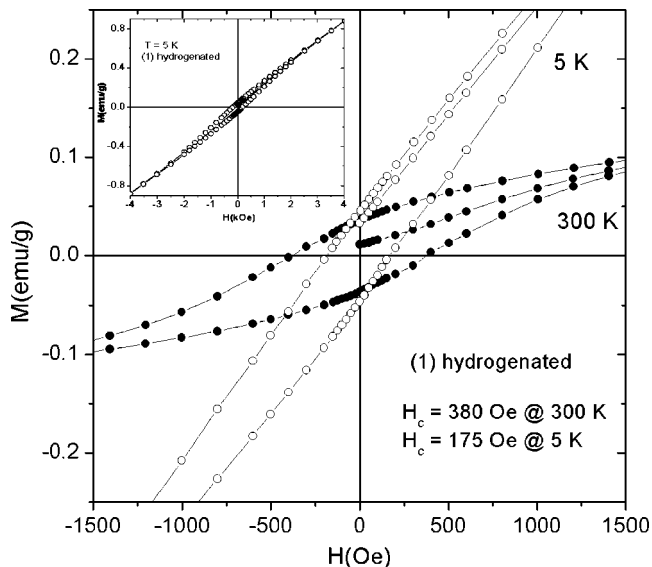
pected for a paramagnet,[12] although the data does not quite fit the Brillouin function (not shown) possibly because of the presence of strong Co^{2+}–Co^{2+} exchange interaction for *T* < 5 K.

To obtain additional information on the nature of the electronic state of Co in samples 1, 2, and 3, we carried out EMR studies at 5 K for the three samples. The observed EMR spectra are shown in Fig. 5, along with the data taken in Co doped with MgO and 1% Co/TiO$_2$ prepared by the sol-gel technique. For the 1% Co/MgO sample, the eight line hyperfine structure centered around $g=4.3$ ($g=$hf/μ_BH) due to Co^{2+} is clearly evident.[13] For 1% Co/TiO$_2$, we observe a similar eight-line patters clearly showing the presence of Co^{2+} ion. For samples 1 and 2, the $g=4.3$ line is still present,

FIG. 2. *M* vs *H* plots at 300 K for the three samples. The inset shows the *M-H* plot of sample 3.
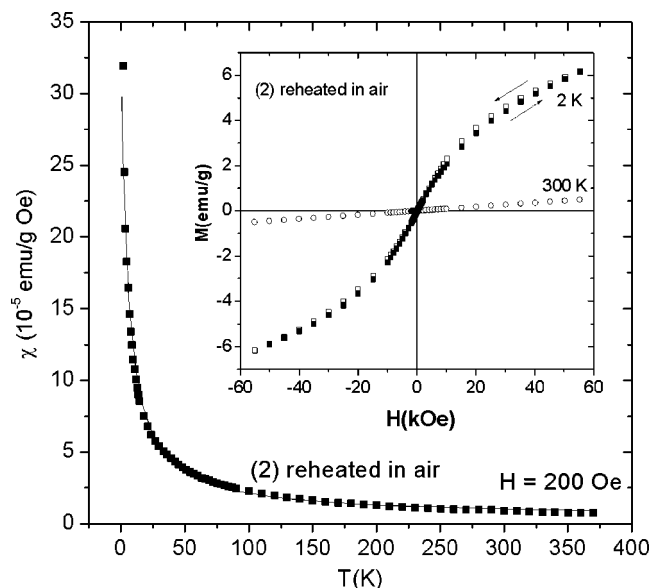

FIG. 4. Temperature variation of the magnetic susceptibility χ for sample 2. The solid line is fit to the Curie–Weiss law: $\chi=\chi_0+C/(T+\theta)$ with $C=1.76 \times 10^{-3}$ emu K/g Oe, $\chi_0=4.55 \times 10^{-6}$ emu/g Oe and $\theta=5$ K. The inset shows the *M* vs *H* variations at 300 and 2 K.
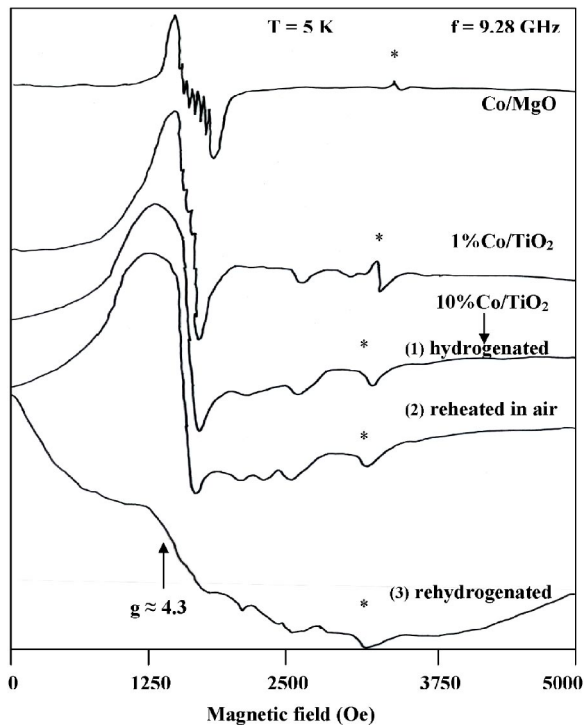
FIG. 5. EMR spectra at 5 K of the various samples shown. The line at g =4.3 is due to Co^{2+} and the line marked with an asterisk is due to an impurity in the sample holder tube.

although considerably broadened and without the hyperfine structure; the latter effects being due to the strong Co^{2+}–Co^{2+} interaction present because of the higher (10%) Co doping of these samples. For sample 3, which was nearly completely hydrogenated as evident from its larger M, we observed a very broad line superposed on which is the weaker g=4.3 line. The additional weaker EMR lines observed in these samples are not yet identified, except the line marked with an asterisk which is due to the background signal from the quartz sample holder. As the temperature of the samples are increased above 5 K, the g=4.3 line becomes weaker disappearing completely above 40 K. This is understandable in terms of the faster relaxation time of Co^{2+} at higher temperatures.[13]

Why does hydrogenation produce RTFM whereas heating in air restores the paramagnetic state? This can be explained if heating in H_2 extracts oxygen from the sample,

producing oxygen holes. These oxygen holes can then provide the necessary exchange coupling between the Co^{2+} ions, leading to the FM state, as suggested by the calculations of Park *et al.*[9] Is the FM state due to Co^0 nanoparticles which are not easily detected by XRD? If Co^0 nanoparticles were present, their oxidation should lead to CoO and Co_3O_4 both of which will show a linear M versus H variation at room temperature, similar to paramagnetism. However, both CoO (Ref. 14) and Co_3O_4 (Ref. 15) are antiferromagnets with Néel temperatures T_N=290 and 40 K, respectively. Therefore, in the χ versus T variations, peaks at their respective T_N's should have been observed in Fig. 4. The absence of these peaks suggests the absence of CoO and Co_3O_4 and consequently Co^0. Therefore, based on the evidence presented in this article, we are led to conclude that RTFM in our hydrogenated samples prepared by the sol-gel technique is not due to Co^0 but it is intrinsic in nature, confirming the model of Park *et al.*[9] and in line with the recent results of Shutthanandan *et al.*[8] in Co-implanted TiO_2 films.

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